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Guidelines for Determination of Laboratory Acceptability for Analysis of Volatile Organic Pollutants Collected on Tenax GC (Trade Name) Adsorbant

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GUIDELINES FOR DETERMINATION OF LABORATORY ACCEPTABILITY FOR ANALYSIS OF VOLATILE ORGANIC POLLUTANTS COLLECTED ON TENAX GC® ADSORBANT

by

W.F. Gutknecht
R.K.M. Jayanty
J.T. Bursey
Systems and Measurements Division
Research Triangle Institute
Research Triangle Park, North Carolina 27709

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EPA Project Officer
Howard Crist

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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The document has two principle parts. The first is a general discussion of the Tenax GC® and GC/MS techniques. Included in this discussion are (1) preparation of Tenax GC® sampling cartridges, (2) sampling with these cartridges, (3) analyte recovery using thermal desorption and (4) qualitative and quantitative analysis using GC/MS. Also included is a general description of a quality assurance program for this analytical effort.

The second principal part of this document provides procedures for evaluating a laboratory's capabilities to utilize the Tenax GC® and GC/MS methods in an acceptable manner. Included are general guidelines for preparation and use of performance evaluation samples and a questionnaire to perform a laboratory system's audit. The techniques presented should also apply to sampling for organic compounds in general using other solid adsorbents.

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SECTION 1
INTRODUCTION

This Technical Assistance Document (TAD) is intended to serve as a guide to those responsible for evaluating and selecting a laboratory to perform sampling and analysis of volatile organic compounds in the ambient air. The sampling and analysis techniques are limited to a discussion of Tenax GC® adsorbant for collection of pollutants and gas chromatography/mass spectrometry (GC/MS) for identification and analysis. Tenax GC® was selected because it is the most widely used medium for sampling of volatile organic compounds in ambient air. However, the techniques presented here are general enough for use with other types of solid adsorbants used to sample for organic compounds and evaluating a laboratory's ability to provide valid air sampling data. It is expected that technical personnel within regional, state, and local environmental regulating agencies will be the primary users of this document.

This document has two principal parts. The first is a discussion of the Tenax GC® and GC/MS techniques to be used for analysis of volatile organic pollutants. The specific analytical procedures discussed include (1) preparation of Tenax GC® sample collection devices; (2) field sampling using Tenax GC® resin; (3) recovery of the organic compounds from the Tenax GC®; and (4) qualitative and quantitative analyses of the compounds using combined gas chromatography/mass spectrometry. This technical presentation is general in nature; that is, specific details of the methods, for example, type of GC column or thermal desorption temperature to be used, are not presented as the methods are in a constant state of improvement. The current literature and experts should be contacted in order to determine the state-of-the-art for the Tenax GC® and GC/MS methods.

The second principal part of this document is a generally objective procedure for evaluating a laboratory's capabilities to utilize the Tenax GC® and GC/MS methods in an acceptable manner. This laboratory evaluation and selection protocol has three principal components.

These are:

(1) Preparation and use of performance evaluation samples for analysis by the laboratory in question.

(2) Evaluation of key personnel function descriptions and written standard operating procedures as provided by the laboratory in question.

(3) A systems audit of the laboratory in question.

This document is not intended to serve as a single source of information upon which all judgements concerning a laboratory's analytical practices can be made. The first part of the TAD should be used as an overview document to be consulted in preparation for a laboratory evaluation, with the user directed to the referenced literature or other specific, detailed information as required. The second part of the TAD, the evaluation protocol, has been made as objective as is reasonable so that it can be used by non-experts. The document, however, does not eliminate the need for sound technical judgement on the part of the person performing the evaluation. In general, persons performing a laboratory evaluation must have a strong chemistry background with some specific knowledge in instrumental sampling and analysis techniques. If such persons are not available, the probability of performing a successful evaluation will be reduced and information obtained inaccurate.

SECTION 2
ANALYTICAL PROCEDURES

ANALYTICAL APPROACH

Tenax GC is a porous polymer based on the structural units of 2,6-diphenyl-p-phenylene oxide. It has a relatively high sorbtive capacity for non- and semi-polar organic compounds and is most useful for collection of C_4 - C_{15} compounds in the boiling point range of 40°C to 200°C.

Volatile organic compounds are concentrated from ambient air onto Tenax GC® in a short, open-ended tube. Tubes made of glass or stainless steel have been successfully used (1-3). Recovery of the volatile pollutants is accomplished by thermal desorption and purging with helium into a cryogenically cooled, capillary trap (1-2,4). The condensed material is revolatilized by heating and the vapors are introduced into a high resolution glass gas chromatography column where the constituents are separated from each other (2,5). Characterization and quantification of the constituents in the sample are accomplished by mass spectrometry either by measuring the intensity of the total ion current signal or by mass fragmentography (2,6).

RANGE AND DETECTION LIMIT

The linear response range for the analysis of volatile organic compounds depends upon several parameters. Included are (1) the contamination found on the "blank" Tenax GC® sampling cartridges; (2) the retention volume of each specific compound collected on the Tenax GC® sampling cartridges; (3) the inherent detection limit of the mass spectrometer for that compound; and (4) the upper limit of ion concentration which results in non-linear response and/or saturates the GC/MS detector. Thus, the range and detection limit are different for each compound present in the original ambient air. The linear range for quantitation on the gas chromatograph/mass spectrometer/computer (GC/MS/COMP) is generally three orders of magnitude. Table 1 lists overall theoretical detection limits for some volatile organic compounds as reported by Pellizzari (7). It must be emphasized that the

TABLE 1. Overall Theoretical Detection Limit of High Resolution Gas Chromatography/Mass Spectrometry/Computer Analysis for Atmospheric Pollutants

Chemical Class	Compound	Estimated Detection Limit[a]	
		ng/m^3	ppt
Halogenated Hydrocarbons	Vinyl bromide	250	57
	Bromoform	0.340	0.03
	Bromodichloromethane	1.300	0.22
	Dibromochloromethane	0.667	0.07
	1-Bromo-2-chloroethane	1.00	0.67
	Allyl bromide	5.00	1.04
	1,2-Dibromoethane	0.530	0.07
	Bromobenzene	0.100	0.02
	Methyl chloride	2000	1000
	Vinyl chloride	800	333
	Methylene chloride	700	200
	Chloroform	200	420
	Carbon tetrachloride	250	400
	1,2-Dichloroethane	32	8.15
	Tetrachloroethylene	2.5	0.38
	1-Chloro-2-methylpropene	62	21.5
	3-Chloro-2-methylpropene	62	21.5
	Chlorobenzene	2.10	0.47
	o-Dichlorobenzene	1.00	0.06
Oxygenated Hydrocarbons	Acrolein	100	56.5
	Propylene oxide	60	25.5
	Butadiene diepoxide	20	6.7
	Cyclohexene oxide	10	2.5
	Styrene oxide	2	0.415
Nitrogenous Compounds	Nitromethane	8	2.4
	Aniline	3.0	0.78
Sulfur Compounds	Diethyl sulfate	50	-
	Ethyl methane sulfate	5.0	-

[a]Limits were calculated on the basis of the retention volume for 2.2 g of Tenax GC®, (at 70°F), capillary column performance and sensitivity of the mass spectrometer to that compound in the mass fragmentography mode of most intense ion (7).

values presented in Table 1 were determined under laboratory conditions. There has been an apparent change in the bulk density of Tenax GC® since using 2.2 g to obtain the values presented in Table 1. With the Tenax GC® currently available, approximately 1.5 g is adequate for a 13.5 X 99 mm sampling tube. The actual detection limits achieved will depend upon the specific sampling and analysis procedures and equipment used. Also, components of field samples such as water vapor, ozone, organic and sulfur compounds will likely affect these limits. Any laboratory performing this type of sampling and analysis should have established the limitations of range and detection for their own Tenax GC® sample collection and GC/MS/COMP sample analysis systems under laboratory conditions. If the Tenax samples are provided to the laboratory for analysis by outside groups, an awareness of these limitations should be reflected in questions on sample information forms; such questions might include volume of air sampled and air temperature.

REPEATABILITY

The repeatability of this method has been determined to vary from ±10 to ±50 percent for different substances when replicate sampling cartridges are examined (5). The inherent analytical errors affecting precision are a function of several factors: (1) the precise measurement of the ambient air sample volumes; (2) the repeatability of thermal desorption for a compound from the tube and its introduction into the analytical system; (3) the repeatability of periodic calibration; (4) the repeatability of transmitting the sample through the high resolution gas chromatographic column; and (5) the day-to-day reliability of the MS/COMP system (1-8).

The accuracy of analyses performed under controlled conditions using laboratory standards is estimated to be in the range of ±30 percent but depends on the compound (2,8). Compounds which are unstable, highly volatile, and suffer from interferences show the poorest accuracy. The accuracy achieved with actual field samples has not been determined.

The repeatability and recovery achieved with representative compounds should be established by a laboratory for its total sampling and

analysis procedures, or at very least, its analysis procedures. Such data should be available in written form and included in any statement of capability.

INTERFERENCES

The potential analytical difficulties with this technique are primarily associated with those cases where isomeric forms of a particular substance cannot be resolved by the high resolution chromatography column and when the mass spectral fragmentation patterns of each of the isomers are identical. An example of such a problem is with the C_5- alkyl aromatics of which there are 53 isomers. As the number of carbon atoms increases in the hydrocarbons and aromatics, the number of potential isomers becomes increasingly large and difficult to completely resolve by gas chromatography and/or by their corresponding mass spectral fragmentation patterns. However, differentiation between the hydrocarbons, that is, alkanes, alkenes, aromatics, oxygenated, etc., can be accomplished.

Operating parameters which provide optimum resolution should be established by the laboratory. An important quality control operation is a regular check of this resolution and, if necessary, corrective action to maintain this resolution.

ARTIFACTS

A problem just beginning to be understood is that of artifacts. "Artifacts" are compounds measured with the GC/MS system which were not present in the original air sample but rather were formed through chemical reactions on the Tenax GC® polymer or within the GC/MS system. For example, unsaturated hydrocarbons adsorbed on the polymer could react with halogens also drawn through the sampling cartridge and form halogenated compounds.

ADVANTAGES AND DISADVANTAGES OF THE ANALYTICAL APPROACH

The gas chromatograph/mass spectrometer is extremely sensitive and specific for the analysis of many volatile organic compounds in ambient air. High resolution gas chromatographic separation provides adequate resolution of the substances found in ambient air for their subsequent

quantification. The combination of the high resolution gas chromatographic column and the selection of specific or unique ions representing the various compounds of interest identified in the air samples yields a relatively specific assay method for these compounds (1 - 8).

The retention volume of any substance on Tenax GC® increases as the ambient air temperature decreases (8). The retention of water by Tenax GC® is low and its thermal stability is high, allowing sensitive analysis (1,2,5,8). Certain questions which still remain to be fully answered regarding the use of Tenax GC® for ambient air sampling are (1) the stability of volatile organic compounds on the adsorbant with time and (2) the release of certain organic compounds from Tenax GC® during sampling and/or analysis.

SAMPLING TUBE PREPARATION

There are several steps to sample tube prepartion including cleaning the Tenax GC®, testing it for suitable quality, and loading the sample collection tubes.

Cleaning Tenax GC®

The adsorbent is placed in open-ended tubes through which air is drawn to collect sample. These Tenax GC®-filled air sampling tubes are often stored in somewhat larger glass tubes with Teflon-lined screw caps after the filling process. Cleaning is accomplished with a Soxhlet extraction apparatus using a series of solvents, such as methanol and pentane, which remove various classes of organic compounds. After extraction, the Tenax GC® is gently dried under conditions which will prevent collection of any new contamination. Since the polymer is easily contaminated, it is imperative that the cleaned sorbent be stored in a very clean container in a clean environment. All glassware and sampling tubes must be thoroughly cleaned before use. This cleaning typically involves washing in soap and water, rinsing with water and various organic solvents, and heating to several hundred degrees Centigrade to ensure removal of all traces of organic compounds. The cleaned glassware should be stored in a chamber purged with air or nitrogen which is free from organic compounds and gloves should be used when handling sample tubes or glassware.

Loading Tubes

Tenax GC® is typically held in place in the tube with glass wool which has been thoroughly cleaned by the same procedure as the resin. The tubes are then conditioned by heating to about 270°C under a helium or nitrogen (ultra high purity) purge for several hours. Open-ended air sampling tubes (Tenax cartridges) are then placed in larger tubes, equipped with Teflon-lined caps. They are labelled and placed in containers. The containers are stored in a freezer at moderately low temperatures, e.g., -20°C. Thermal desorption of Tenax GC® tubes just prior to sample collection is strongly advised. As with the storage of the Tenax GC® itself, the environment for storage of the loaded sampling tubes should be "free" of all organic compounds which might contaminate the filled cartridges. It is generally recommended that sampling and analysis be completed within four (4) weeks after preparation of the cartridges.

Quality Control

Before the laboratory accepts a batch of polymer from a supplier, approximately ten (10) grams from a single lot should be cleaned and analyzed for contamination. Analysis by GC/FID should be performed on two or three samples after cleaning and on three (3) sampling tubes after storage for several days following cleaning. The background levels of organic compounds on Tenax sampling tubes can be checked by desorbing the tubes with a thermal desorption apparatus attached to a gas chromatograph equipped with a FID detector and capillary column.

To determine background contamination, the total integrated peak areas are used to determine acceptability. This total area should be a small fraction of the area resulting from measurement of the lowest concentration level of the calibration mixture. It would also be advisable to routinely check the bulk density of Tenax GC® as part of the acceptance testing.

As part of the quality control procedures, sampling protocols and chain of custody forms should be prepared for each sampling tube. The history of each sampling tube should be traced from the time it is prepared until the data has been reduced to a finished form.

A certain number of Tenax sampling tubes should be set aside as blanks. A reasonable number would be one blank for 15 or fewer field samples and, thereafter, at the rate of one blank per 15 samples. These sampling tubes should travel to the field site and be returned to the laboratory to be analyzed along with the field samples. Spiked samples may be prepared by fortifying the Tenax cartridges with known concentrations of selected analytes. During analysis of field samples at least one spiked sample should be analyzed per instrument per day. A certain number of duplicate samples may be collected and one of the duplicate pairs sent to an independent laboratory for corroborative analyses. All Tenax sampling tubes should be kept in a freezer until analyzed.

SAMPLE COLLECTION

For collection of air samples, it is important to realize that the total volume of air sampled may cause the elution of compounds from the sampling tube. These retention volumes have been determined under laboratory conditions for a number of organic pollutants (2,9). Examples of retention volumes determined as a function of temperature are presented in Table 2.

Retention volumes vary widely from compound to compound. Collection of a large volume of air to determine a compound present at a low atmospheric concentration could result in significant losses of other compounds with low retention volumes. The retention volumes listed in Table 2 were determined in the laboratory using single compounds at constant humidity and temperature.

Retention volume is generally defined as the air volume at which one-half of the concentration entering the sampling tube elutes from the other end of the tube. Retention volumes do not reflect the variable sampling conditions or complex chemical environment which would be encountered during field sampling (10). Consequently, the values in Table 2 should be interpreted only as estimations of actual retention volumes under field sampling situations. It is therefore not considered valid to use these retention volumes to correct field sample data for compound losses.

TABLE 2. Tenax GC Retention Volumes for Several Atmospheric Pollutants[a]

Chemical Class	Compound	b.p. (°C)	Temperature (°F) 60	80	100
Halogenated Hydrocarbons	methyl chloride	-24	6	4	2.5
	vinyl chloride	13	1.5	1.0	0.6
	methylene chloride	41	9	5	3
	chloroform	61	31	18	10
	carbon tetrachloride	77	27	16	10
	1,2-dichloroethane	83	41	23	14
	tetrachloroethylene	121	267	144	78
	allyl chloride	45	16	9	5
	chlorobenzene	132	653	344	181
	o-dichlorobenzene	181	1,153	656	372
	benzyl chloride	179	2,061	1,125	612
	bromobenzene	155	1,521	764	384
Oxygenated Hydrocarbons	acrolein	53	14	8	4
	propylene oxide	34	24	11	5
	phenol	183	1,490	769	398
Esters	ethyl acetate	77	108	48	22
	methyl acrylate	80	111	50	23
	methyl methacrylate	100	484	209	90
Ketones	acetone	56	17	8	4
	methyl ethyl ketone	80-2	57	27	13
Aldehydes	acetaldehyde	20	2	1	0.7
	benzaldehyde	179	5,152	2,382	1,101
Alcohols	methanol	64.7	1	0.6	0.3
	n-propanol	97.4	20	10	5
	allyl alcohol	97	23	11	6
Aromatics	benzene	80.1	77	38	19
	toluene	110.6	348	173	86
	ethylbenzene	136.2	984	487	243
Hydrocarbons	n-hexane	68.7	23	12	6
	n-heptane	98.4	104	55	29
	2,2-dimethylbutane	49.7	0.4	0.2	0.1
Inorganic Gases	nitrogen dioxide	-	0	0	0
	sulfur dioxide	-	0.05	0.02	0.01
	water	100	0.05	0.03	0

[a]Retention volume is given in ℓ/2.2 g Tenax GC® used in sampling cartridges.

Another way to deal with uncertain retention volumes is to spike a few of the sampling tubes with deuterated analogs of the target compounds before sampling. These tubes can then be used in the field along with the unspiked tubes. The deuterated analogs are recovered and quantified along with the compounds collected in the field. The loss of the deuterated compounds can be compared to that expected from laboratory retention volume studies. Statistically significant differences between retention volumes thus measured and expected are attributed to premature breakthrough and corrections can be made to the field-collected compound results. However, this approach requires the assumptions that (1) no unlabelled substance is generated as the result of artifact reactions and (2) no contamination has occurred. Walling (11, 12), has used four co-located samplers operated simultaneously and at widely different flow rates to aid in the evaluation of data from Tenax samples. In this sampling arrangement, a decrease in calculated concentrations of a compound from one air sample volume to the next higher one may indicate that breakthrough or some other complication has occurred. The use of tandem collection tubes in this approach provides additional evidence that breakthrough occurred if compounds are detected on the back-up cartridge and addition of the values produces constant results. However, in the case of certain aromatic compounds such as benzene and toluene, this approach suggests the possible generation of these compounds during sampling. With very complex or poorly defined sampling environments, exploratory sampling and analysis may be necessary before quantitative work can be done.

Sampling Operation

Samples may be collected individually using personal monitoring pumps or several at a time using a large pump attached to a multi-port manifold. When using a sampling manifold, flows through the sampling tubes could be controlled by critical orifices, micro-valves or similar flow control devices. The flow rates will be set (if necessary) or measured at the beginning of the sampling period, measured once during the period if the period is long, and again at the end of the period. The flow rates may be measured with a calibrated rotameter. Flow rates

are typically in the range of 10-400 mL/min for a 12 hour collection period.

The sampling train for open-ended tubes consists of a Tenax sampling tube secured with Teflon fittings (Beckman) at both ends. The upstream fitting is open or attached to a sample collection probe; the downstream fitting consists of a union for attachment of a tube connected to a personal sampling pump or a flow controller which, in turn, is attached to a sampling manifold.

The Tenax cartridges should be placed into and removed from the sampling train without direct contact by hands or any surface which might cause contamination. The length of time when the ends of the tube are open and the tube is not in the train or its larger storage tube should be minimized, especially in a field environment. After sample collection, the Tenax cartridges are placed in the larger tubes which are closed and placed in the container used to bring the cartridges into the field.

Previous experiments have shown that many volatile organic compounds collected on Tenax GC® sorbent are sufficiently stable for adequate recovery from the cartridge samplers for approximately four (4) weeks after sampling when they are kept in tightly closed tubes placed in a second container which can be sealed, protected from light and stored at -20°C. Additional studies will possibly define storage parameters which may result in more precise recoveries.

ANALYSIS

The analysis of the samples collected involves two principal operations. These are recovery of the organic compounds by thermal desorption and measurement using GC/MS.

Recovery

The organic compounds are recovered from the Tenax sample tube by heating and then collecting in a cryogenic trap before introduction into the GC/MS system (1,2,5). The thermal desorption chamber and a valve to control gas flows are heated to a temperature high enough to prevent condensation but not so high as to cause decomposition. In a typical thermal desorption cycle, a sampling tube is placed in the

preheated desorption chamber and the helium gas is channeled through the tube to purge the vapors into the liquid nitrogen-cooled capillary trap. After the desorption has been completed, the valve is rotated and the temperature on the capillary trap is rapidly raised (usually greater than 100°/min.); the carrier gas then introduces the vapors onto the high resolution GC column. After all the components have eluted, the column is cooled to ambient temperature and the next sample is processed. Because of dead volume existing in the desorber and transfer lines, cryofocusing on the head of the GC column may be necessary.

Calibration

Calibration is typically performed in one of two different ways. In one approach standard mixtures of the compounds of interest are prepared and used for direct injection; the responses acquired are used to prepare a conventional calibration curve. In the other approach internal standards are used and concentrations are calculated using relative responses. This approach requires a demonstration of the linearity of the particular spectrometer over the entire range. Non-linearity requires calibration curves.

In one approach to direct calibration, a liquid aliquot of an organic compound of interest is injected into a helium-filled container through a septum cap (13). A large number of different compounds may be injected. The bottle is agitated and heated to achieve complete vaporization. The weight of each compound delivered to the tube is calculated from (a) the density of the liquid, (b) the volume of liquid injected into the known volume of the bottle, and (c) the volume of vapor injected into the tube. This standard gas mixture is injected directly into the GC/MS system for calibration.

A second approach to generating the standard gas mixture is through the use of permeation tubes (14). A permeation tube consists of a closed container, part of which is permeable to some substance contained inside it. The volatile compound permeates through this part from which it evaporates (in most cases) at a constant rate if temperature is constant. The vapor generation rate is determined by weight loss. In a typical system, the permeation tubes are placed in a therm-

ostated glass chamber through which nitrogen or air flows at a known rate. The combination of permeation rates for the tubes and the flow rate allows calculation of concentrations. Further dilution may be performed if necessary. The standard gas mixture so generated may be used for direct injection into the GC/MS system or injection into a Tenax sampling tube.

A third approach to generating a standard gas is flash evaporization, with immediate collection on Tenax GC®. In this process, the organic compound(s) (liquid, or solid in solution) is/are injected into a heated stainless steel or glass tube having clean air or helium passing through it. The exhausting gas is passed directly into a Tenax air sampling tube whereupon the compounds are collected; tubes loaded in this manner are then used as standards. However, such a calibration is not directly nor easily useful if a different adsorbant is used.

With the indirect method of calibration, the responses of the compounds of interest are measured relative to a marker compound which is not found in ambient air (15). In this approach standard atmospheres of the compounds of interest are prepared using the static dilution bottle or permeation tube methods. The responses of these compounds are then measured relative to an internal standard such as perfluorotoluene (PFT) using the GC/MS system. As a precautionary measure the response of each compound should be checked for constancy over the concentration range of interest. Known amounts of PFT are then injected into the Tenax sample tubes after field sampling and prior to thermal desorption and GC/MS analysis. The PFT is measured along with the compounds collected and these latter compounds are quantified (5).

GC/MS Measurement

A capillary column interfaced to a GC/MS is used for resolving the volatile organic compounds (5).

The mass spectrometer is usually first set to operate in the repetitive scanning mode. In this mode the ion separation unit of the MS is automatically scanned exponentially upward from a preset low mass to a high mass value. Although the scan range may be varied depending

on the particular sample, typically the range is set from approximately m/z 35 to m/z 350. After completion of the scan, the instrument automatically resets itself to the low mass position in preparation for the next scan, and the information is accumulated by an on-line computer and written onto magnetic tape or disk. A continuous scan cycle is maintained and repetitively executed throughout the chromatographic run. The result is the accumlation of a continuous series of mass spectra throughout the chromatographic run in sequential fashion.

Prior to analysis of unknown samples, the system mass-determination function is calibrated by introducing a standard substance, such as perfluorokerosene, into the instrument and determining the time of appearance of the known standard peaks in relation to the operating point of the ion separation unit. The mass calibration curve thus generated is stored in the computer memory. This calibration serves only to calibrate the ions over the scanning range.

While the ion separation unit is continuously scanning, the sample is injected and automatic data acquisition is initiated. The data treatment occurring during data acquisition will depend upon the MS/COMP system in use. Most systems, however, are set to recognize and store information about each mass spectral peak which exceeds a preset threshold intensity.

This procedure continues until the entire GC run is completed. By this time there are from 800-1400 spectra on the magnetic storage media which are then subsequently processed. Depending on the information required, they may then either be processed immediately or additional samples may be run, stored on magnetic tape or disk and the results examined at a later time.

The mass spectral data are typically processed in the following manner. First, the original spectra are scanned and the total ion current (TIC) information is extracted. Then the TIC intensities are plotted against the spectrum number on a plotter to obtain a gas chromatogram. The information will generally indicate whether the run is suitable for further processing, since it provides some idea of the number of unknowns in the sample and the resolution obtained using the particular GC column conditions.

The next stage of the processing usually involves the conversion of the spectral peak times to peak masses which is done directly. The mass conversion is accomplished by use of the calibration table obtained previously using perfluorokerosene.

After the spectra are obtained in mass-converted form, processing proceeds either manually or by computer. Fully computerized interpretations are preferred. In the manual mode, the full spectrum of scans for the GC run is recorded on a plotter. The TIC information available at this time is most useful for deciding which spectra are to be analyzed. At the beginning of the run where GC peaks are very sharp nearly every mass spectrum must be inspected individually to determine the identity of the compound. Later in the chromatographic run when the GC peaks are broader only selected scans need to be analyzed.

Identification of the resolved compounds from data produced by the mass spectrometer can be performed in a variety of ways including: (1) manual interpretation; (2) comparing the fragmentation patterns of the unknown mass spectra to an eight major peak index of mass spectra (16); and (3) comparing the fragmentation patterns of the unknown mass spectra to those in various computer libraries of mass spectral data. When unusual certainty is needed the identification of unknowns can be confirmed by comparing the fragmentation pattern and elution temperatures for two different chromatographic columns (e.g., SE-30 and Carbowax SCOT capillaries) for the unknown and authentic compounds. This procedure requires, however, that duplicate samples be collected.

In many cases the estimation of the level of pollutants by capillary gas chromatography in combination with mass spectrometry is not feasible utilizing only the total ion current monitor. Since baseline resolution between GC peaks is not always achieved, techniques have been developed whereby full spectra are obtained during the chromatographic separation step and selected ions are presented as mass fragmentograms using computer software programs which allow the possibility of resolving constituents which were not resolved in the total ion current chromatogram (6). In this approach fragmentograms for any combination of ions are requested from the computer when full mass

spectra have been obtained during chromatography. Thus selectivity is obtained by choosing characteristic ions for a particular organic substance. The total ion intensity of the characteristic ions is plotted and this intensity versus time is subsequently used for quantification. Also quantification with external standards is easily achieved using the intensity of the total ion current monitor or characteristic ions in the mass spectrum of the external standard. Thus, mass fragmentography can be used for the quantification of organics in ambient air when the total ion current monitor is inadequate because of the lack of complete resolution between components in the mixture. This is usually done in an automated manner and is the reason for using a mass spectrometer rather than a more economical non-specific detector or the mass spectrometer total ion current.

LABORATORY QUALITY ASSURANCE PROGRAM

A rigorous quality control/quality assurance program (QC/QA) is essential for satisfactory sampling of volatile organic air pollutants using Tenax GC® and analysis by GC/MS. It is expected that any laboratory being considered for this effort will have such a program in place. Regardless of the size and sophistication of this QC/QA program, certain characteristics are desirable to assure that high quality, useful data are obtained. The most desirable characteristics of the QC/QA program are described by subject area in the following.

Organization

A detailed organizational structure should exist which clearly delineates each person's duties and responsibilities so that someone outside of the organization can determine who is responsible for each activity. Effective lines and methods for communication between individuals in different parts of the organization should be established to ensure that all objectives of the sampling and analysis program are met. Effective lines of communication are also essential for bringing analytical problems to the attention of management. One individual should be assigned overall responsibilty for QC/QA with direct access to management.

Personnel Experience/Training

A training program should be established, which company personnel must complete before being qualified to perform assigned tasks without constant supervision. This program should be under the direction of a specific person(s) and a written record of training accomplishments kept for each individual. Ideally, the proficiency of technical personnel should be periodically reviewed in some planned manner and the results documented. Current periodicals such as The Journal of the Air Pollution Control Association, Environmental Science and Technology, Analytical Chemistry, etc., should be circulated among the staff with encouragement to read them. Personnel should be encouraged to participate in certification/ audit programs, workshops, conferences and training courses and the results documented

General Operating Procedures

The laboratories should be maintained in a neat and orderly manner. All chemicals used as standards and for other purposes should be properly labeled (including the date received in the laboratory) and stored so as to prevent contamination or loss. A record should be kept on the receipt of all chemicals, reagents and gas cylinders with the expected shelf life recorded on this same label. Usage logs should be kept for all equipment and all equipment should receive regular maintenance.

Standard operating procedures should be available in writing for personnel who routinely perform the activities of sampling, shipping, storage and analysis. Changes in these procedures should be fully documented. Files of all procedures and changes in procedures should be maintained. The history of a sample (sample identification, chain-of-custody, analysis and sampling methods used, calibration curves, QC/QA procedures used, calculations, record-keeping, etc.) should be clearly documented, dated, and maintained in an organized manner so as to be easily followed by someone who did not actually collect or analyze the sample.

Sampling and Analysis

The sampling and analysis procedures should include a full complement of QC/QA components. Operational checks should be performed to verify that proper assembly of the sampling equipment has occurred. Operational checks also should be performed on the GC/MS on a daily basis. Standard operating procedures for sampling and analysis should be developed in writing. These procedures should include QC/QA operations which are required components of the total procedures.

Calibration procedures and schedules should be established for all important sampling and analysis equipment and stored in a permanent file. When equipment is calibrated, a logbook and/or data form should be made which contains the name of the person doing the calibration, the date of the calibration, and the calibration factors determined. Calibration and reference standards should be traceable to the US Environmental Protection Agency (USEPA), National Bureau of Standards (NBS) SRM, or other recognized standards such as ACS, whenever possible. Calibration records should be maintained in an organized file for a reasonable amount of time, e.g., two years. QC samples used regularly should include field blanks, laboratory blanks, field replicates, spiked field samples and performance check samples.

Data Reduction and Validation

An effective quality assurance program will ensure that all samples are subjected to data validation techniques which are adequate for the intent of the sampling results and compatible with the type of sample (routine, nonroutine). For example, for routine samples (similar samples collected and analyzed more often than every 4 to 6 weeks) quality control charts such as those described in the Quality Assurance Handbook (17) may be appropriate. The basic idea of control charts is to determine the normal limits (precision) associated with the sampling results (based on the past performance of the laboratory) so that sample data which fall outside these limits can be scrutinized to determine the source of the imprecision (error). Standard samples or control samples are generally used to establish these limits and the long-

er a specific control chart is used, the easier it becomes to identify erroneous data.

When used in conjunction with the Method of Standard Additions (spiking), control charts can be very effective in identifying erroneous results, particularly those associated with the analysis of the sample. Errors resulting from mistakes made in the field, however, may not be identified by this approach since many sources do not emit a constant level of pollutant over long periods of time. For best results the standards should be carried through the entire analytical procedure when utilizing this approach. Control charts may not be cost-effective on samples collected at infrequent intervals; thus the use of Standard Additions or control samples may be adequate. This latter method alone will tend to identify incorrectly prepared standards and other laboratory errors but will not identify errors made during sample collection.

Some examples of good data reduction and validation practices are:

- All laboratory and field data sheets are completed, dated and signed by the analysts/operator and checked or reviewed by management personnel. Data sheets should be filled out in ink (not pencil).
- Standard written procedures, forms, etc., are used to perform necessary computations, data reductions, and validations.
- The company has a specific policy for reporting data, including the number of significant figures and detection limits.
- Preventive maintenance schedules are established for each important physical (electrical, electronic, mechanical) portion of equipment which could affect the validity of the results or cause delays at the test site.
- There is an established closed-loop system to ensure that corrective actions are taken when problems or out-of-control conditions are detected and reported.
- Problems which have been discovered and corrected are recorded in a consistent manner stating the deficiency, the corrective action taken, and the date of the action.
- Independent, duplicate checks are frequently made of the key aspects of the sampling and measurement systems.

- Quality assurance samples are periodically introduced (unidentified as quality assurance samples) into the analytical system.
- The company participates in external performance audits that are relevant to the test methodology.

Record Keeping

A field logbook or "events log", recording field measurements and other pertinent observations, should be maintained in ink by the sampling team. This may consist only of a binder containing all the data sheets necessary for recording the test data, but many companies find it beneficial to have logbooks for the sampling operator, the recovery team and the analyst.

The secondary containers in which the Tenax sampling tubes are stored should be labelled in a permanent manner with an identification number, the date, time, and sampling location and name of the person who collected the sample. A sample custodian should be appointed who will keep a record of samples submitted, dates received and analyzed, sample storage techniques used and analyses done, including procedures used and the person responsible.

Standardized forms are used whenever practical to ensure that all required data are collected and recorded. Forms should be developed and used for the following:

- Records of preparation of individual Tenax sampling tubes
- Records of QC checks on Tenax GC® resin
- Records of sample collection and storage
- Records of GC/MS maintenance
- Records of GC/MS calibration data
- Records of QC tests of the GC/MS analysis system
- Records of GC/MS field sample analysis data

All records including standard operating procedures, QC/QA procedures, corrective action requests, etc., should be organized and accessible; that is, a document control or management system should be in place.

Performance and Systems Audits

A laboratory should be a regular participant in round robin studies and others which involve analysis of known samples from external sources. These serve to uncover problems sometimes missed with in-house quality assurance samples which might be inadvertently prepared with some bias.

Performance and systems audits by external groups should be welcome as a means of uncovering problems and improving in-house procedures.

A laboratory should designate one individual to serve as the quality assurance officer for each project. The manager may have to assume this role in a small company. This individual should perform routine systems audits of the laboratory including the sampling and analysis operations. He should also supply unidentified quality assurance samples to the analysts on a routine basis to check performance.

Data Assessment

Methods of data assessment should be established in writing for each project. The validated data should be evaluated for outliers Following this test, precision (from replicate analyses) and recovery (from spiking experiments) may be calculated. Sample source comparability may be tested through application of the F and Student's t tests.

Corrective Action

Problems uncovered through systems and performance audits, evaluation of QC sample analysis results, and alertness and concern on the part of the analysts should result in immediate corrective action. A form should be available which indicates the nature of the problem, the corrective action to be taken, and what and when corrective action was taken. Management should be informed when such action is taken.

Corrective action may include but is not necessarily limited to: recalibration of the GC/MS; replacement of Tenax GC® which gives unacceptable blank values; additional training of laboratory personnel; re-

pair of sampling and analysis instrumentation; and identification of source(s) of loss or contamination.

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SECTION 3
EVALUATION PROTOCOL

INTRODUCTION

This section presents criteria for evaluation of a laboratory's capability to perform acceptable determinations of volatile organic pollutants in ambient air collected on Tenax GC® resin. Evaluation of this capability can be accomplished in three phases.

(1) Analysis of Performance Evaluation (P.E.) samples by the subject laboratory.

(2) Evaluation of key personnel function descriptions and written Standard Operating Procedures (S.O.P.'s) as provided by the subject laboratory.

(3) Systems audit of the subject laboratory

Overview of Performance Evaluation (P.E.) Sample Analysis

Prior to award of a contract or issuance of a work order, the laboratory should demonstrate its ability to perform analyses of the types of samples to be collected in the field. Analyses of the P.E. samples will allow the regulating agency to determine whether the laboratory's personnel fully understand the required analytical methods and whether the methods can be performed using their own equipment.

The P.E. samples are designed to test the capabilities of the laboratory in the following areas:

- Identification and quantification of hazardous organic substances
- Precision and accuracy of analytical data
- Limits of detection of the laboratory's equipment
- Ability to maintain a contamination-free environment
- Ability to perform computerized mass spectral library searches

- o Understanding of documentation requirements
- o Understanding of reporting requirements

Overview of Evaluation of Laboratory-Supplied Documentation

Prior to award of contract or issuance of a work order, the laboratory should provide documented evidence that it has the personnel and procedures in place for successful performance of sampling and analysis. This documentation is least important of the three evaluation components and could be considered optional. Examples of documentation which could be requested include the following:

- o Functional descriptions of key personnel, and
- o Standard Operating Procedures for:
  - (1) Sample receipt, handling, storage and control
  - (2) Security, chain-of-custody and document control
  - (3) Sample analysis
  - (4) Calibration, standards traceability
  - (5) Ongoing routine laboratory operations (including copies of latest instrument maintenance logs)
  - (6) Laboratory safety
  - (7) Laboratory QA/QC (including procedures for in-house audits)

It should be noted that such documentation should not be required to conform specifically (i.e., in every detail) to the agency's requirements but it should be representative of standard laboratory operations and should give clear evidence of the laboratory's ability to successfully perform the required sampling and analyses.

Overview of Laboratory Systems Audit

When a laboratory has successfully demonstrated the ability to analyze Performance Evaluation samples and report data acceptably, and when the regulating agency has reviewed and approved laboratory-supplied documentation, the laboratory may be subjected to a site evaluation or systems audit. The purpose of this audit is primarily to verify the laboratory's claims as represented in the supplied

documentation. It also serves as a mechanism for performing several important secondary functions. These include:

- o Presentation of project goals
- o Dicussion of weaknesses identified through P.E. sample analysis
- o Identification of correctable weaknesses in the laboratory facility, and
- o Establishment of a baseline for further laboratory audits.

PERFORMANCE EVALUATION SAMPLES ANALYSIS

P.E. Sample Preparation

The P.E. samples should be prepared by the regulating agency or a contractor with experience in preparation of quality assurance samples using Tenax GC®. Typically two sets of samples would be provided to the laboratory for analysis. Sample Set A would consist of one or more Tenax sampling tubes fortified with known quantities of organic compounds. These tubes should be further fortified by the subject laboratory with material provided, and then analyzed to test fortification and tube handling capability. Sample Set B would consist of two or more tubes fortified with known, replicate quantities of organic compounds. The tubes should be analyzed by the subject laboratory and the results used to determine laboratory precision. Blank Tenax sampling tubes should be provided to the laboratory for analysis, and finally, the laboratory should provide to the agency several blank Tenax sampling tubes which it has prepared. These latter tubes should be tested for cleanliness by the agency or another qualified laboratory.

The compounds used to fortify the P.E. samples should be selected by the regulating agency. These could be selected from several lists including:

- o The Hazardous Substance List (Resource Conservation and Recovery Act, Subpart C, Appendix VIII).
- o Compounds expected in the air at the sites to be sampled.
- o Compounds which sometimes are found as contaminants in Tenax GC® analysis.

Three (3) to ten (10) compounds should be loaded on each Tenax P.E. sample tube and the compounds should be distributed among the chemical classes normally collected on Tenax GC® polymer; compound selection should be biased towards those compounds expected to be emitted from the site(s) to be sampled. Concentrations should range from near the detection limit for some to approximately fifty (50) times the detection limit for others. These detection limits are to be determined by the group preparing the P.E. samples.

P.E. samples should be generated using techniques described earlier for spiking and calibration. Test atmospheres should be generated by vaporization of a known amount of a neat sample in a glass bulb, with a permeation tube system or by flash vaporization. Known volumes of the standard atmosphere should be drawn through or loaded by injection into the Tenax GC® polymer. These tubes along with unspiked tubes should be submitted to the subject laboratory for analysis. The group preparing the P.E. samples has the responsibility for providing the regulating agency with analytical acceptance criteria for each compound in the P.E. sample. Included are detection limits, accuracy and precision. These criteria are to be based on the state of the art at the time of the evaluation and also guidelines provided by the USEPA.

Sample Set A

Sample Set A is intended to test the subject laboratory's capability to fortify Tenax sampling tubes. The laboratory would be provided with one or more tubes loaded with known quantities of volatile organic compounds. A liquid mixture of some of these same compounds plus others would be provided to the subject laboratory. The laboratory would be instructed to load a known mass of this mixture in gas form onto the tube(s) without knowing the quantities of each component in the mixture. This spiking would need to be performed using the glass bulb or flash vaporization techniques. (Laboratories unable to use these techniques would analyze Sample Set A without fortification.) The tubes fortified by the laboratory would then be analyzed and the analysis results reported using Performance Evaluation Sample Information-Table 1. The evaluator would calculate the recoveries of the

compounds spiked unto the Tenax sampling tubes and present this in P.E. Sample Information-Table 2. Blank tubes would be analyzed and the compounds determined reported using Table 1; the evaluator would then complete Table 4. Detection limit and accuracy criteria are also to be entered on these forms. In addition to the forms described, the subject laboratory should provide supporting data including total ion current, mass chromatograms and mass spectra. The quality of the supporting data is to be judged by comparison to examples provided in Appendix B.

Sample Set B

The Tenax tubes in Sample Set B should be quantitatively analyzed for volatile organic compounds. Blanks should be analyzed and all results reported using Performance Evaluation Sample Information-Table 1. The evaluator would use these data to complete Tables 3 and 4. Again performance criteria are to be placed on the tables by the evaluator and supporting data are to be evaluated following the examples presented in Appendix B.

Scoring

The results reported on the Performance Evaluation Sample Information tables are to be reviewed and judged for acceptability by the regulating agency or its designated experts. The regulating agency may wish to make comparisons if several laboratories are being considered for performance of a sampling and analysis effort.

TABLE 1

PERFORMANCE EVALUATION SAMPLE INFORMATION
QUALITATIVE AND QUANTITATIVE ANALYSES

SAMPLE SET _____
P.E. Sample No. _____

Organic compound	Identified by lab. Yes	No	Mass loaded on Tenax GC®	Quantity reported by laboratory	Quantitative acceptance criteria window	Quantitative analysis acceptable Yes	No

TABLE 2

PERFORMANCE EVALUATION SAMPLE INFORMATION

Laboratory Spikes - Sample Set A

P.E. Sample No._____

Organic compound	Amount spiked	Amount recovered	Percentage recovered	Acceptance criteria window	Recovery acceptable? Yes	No

TABLE 3

PERFORMANCE EVALUATION SAMPLE INFORMATION

P.E. Sample No._____

Organic compound	First analysis result	Duplicate analysis result	Precision	Acceptance criteria window	Precision acceptable Yes	No

TABLE 4

PERFORMANCE EVALUATION SAMPLE INFORMATION

Reagent Blank - Sample Set A____, B____

P.E. Sample No. _____

Organic compound identified	Mass of compound measured	Detection limit of compound	Blank level acceptable? Yes	No

EVALUATION OF LABORATORY SUPPLIED DOCUMENTATION

Each laboratory should submit documentation indicating that it has the personnel and internal procedures in place for successful performance of the Tenax GC® sampling and GC/MS analysis. The evaluator or regulating agency should review the documentation provided by the laboratory and check for the items below.

Key Personnel

	Documentation Provided? Yes	NO
(1) Functional description of overall contract manager.	___	___
(2) Functional description of sample custodian.	___	___
(3) Functional description of quality assurance officer.	___	___
(4) Functional description of Tenax GC® specialist.	___	___
(5) Functional description of GC/MS operator.	___	___
(6) Functional description of MS data interpreter.	___	___

Standard Operating Procedures

Standard Operating Procedures (SOP's) for several relevant laboratory operations which could be requested include:

	Documentation Provided? YES	NO
(1) SOP for GC® Tenax preparation.	___	___
(2) SOP for standard preparation.	___	___
(3) SOP for spiking samples.	___	___
(5) SOP for GC/MS operation.	___	___

SYSTEMS AUDIT

The third phase of the evaluation is a systems audit using the questionnaire in Appendix A as the basis for this audit. The systems audit is intended to verify that the laboratory has the personnel, equipment, and internal procedures in place for successful performance of the sampling and analyses. Topics in the systems audit include:

- o Organization and responsibility
- o Analysts' training
- o Sample handling and custody
- o Equipment maintenance
- o Laboratory orderliness
- o Instrument calibration
- o Operating procedures
- o Quality control
- o Corrective action
- o Record keeping

Much of the information required may be obtained from the documentation supplied by the subject laboratory. This information should be verified and additional information collected and verified through a visit to the laboratory. The information required is presented in the questionnaire. The evaluator should read through the documentation provided by the subject laboratory and answer as many questions as possible with information taken from the documentation. When this has been completed, the evaluator should make arrangements with the laboratory for the on-site visit. Indicate to the laboratory, the intention of the visit and the structure of the audit, which should include the following:

- o Meeting with management
- o Tour of the laboratory and inspection of equipment
- o Review of MS data handling procedures
- o Review of records and record keeping procedures

The laboratory should have available for the auditors copies of all forms, logbooks, and other written material used in similar analy-

sis programs. The analysts who perform the various laboratory functions should be available for discussions with the auditors.

Using the Audit Questionnaire

Included in Appendix A is the audit questionnaire. The questions should be answered as completely as possible using the documentation provided by the subject laboratory. Those questions which are considered important to the success of the project may be posed to the appropriate laboratory personnel during a site visit. Note that in some instances, certain information is requested rather than simple yes/no answers. The quality of the laboratory as determined through use of this questionnaire should be judged by the staff of the regulating agency or their qualified contractor.

APPENDIX A

Laboratory Systems Audit Questionnaire

LABORATORY SYSTEMS AUDIT QUESTIONNAIRE

Organization and Responsibility

Enter the names of the following designated individuals:

(1) Project Manager _____

(2) Laboratory Supervisor _____

(3) Technical Project Supervisor _____

(4) Quality Assurance Officer _____

(5) Sample Custodian _____

(6) Tenax GC® Specialist _____

(7) GC/MS Specialist _____

(8) MS Data Interpretation Specialist _____

(9) Person Responsible for Data Review and Validation _____

(10) Laboratory management structure. Sketch a diagram of the laboratory organization.

Communication

(1) Lines of communication: Enter the names of persons in the following positions and use lines and arrows to indicate the lines of communication.

_____
Technical Supervisor

_____
Laboratory Manager

_____
Analyst

_____
Ouality Assurance Officer

_____
Analyst

_____
Analyst

_____
Data Review and Validation

(2) Sources (i.e., papers, books, manuals) of technical guidance

_____

_____

_____

_____

Experience of Personnel

(1) The responsible analyst has ____ months of experience in preparation of Tenax GC® cartridges and can demonstrate such preparation.

(2) The responsible analyst has ____ months of experience in fortification (spiking) Tenax GC® with volatile compounds and can demonstrate such preparation.

(3) The responsible analyst has ____ months of experience in the preparation of standard gaseous mixtures of organic compounds and can demonstrate such preparation.

(4) The responsible analyst has ____ months of experience in thermal desorption and cryogenic trapping of volatile organic compounds.

(5) The responsible GC/MS operator has ____ months of experience in operation of a GC/MS/DS.

(6) The responsible MS spectral interpreter has ____ years of experience in this function.

(7) The responsible Ouality Assurance Officer has ____ years experience in OC/QA.

(8) The responsible Sample Custodian has ____ months of experience.

(9) The overall contract manager has managed ____ or more analytical contracts.

(10) The Quality Assurance Officer has served as same for ____ or more other contracts.

Laboratory Operation	YES	NO
(1) The analysts have their own copies of the standard operating procedures.	___	___
(2) The analysts have their own copies of the instrument performance data.	___	___
(3) The analysts have their own copies of the latest monthly QC plots.	___	___
(4) The analysts are aware of the most recent control limits.	___	___
(5) The analysts have copies of the lists of samples in-house to be analyzed.	___	___
(6) The analysts have their own copies of safety instructions.	___	___
(7) The majority of the personnel are aware of the contamination and stability problems associated with Tenax GC®.	___	___

Facilities	YES	NO
(1) Laboratory has a toxic substances handling facility and personnel trained in the use of this facility.	___	___
(2) Separate space is provided for preparation of clean Tenax GC®.	___	___
(3) Facility for spiking Tenax GC® sampling cartridges is free of solvents and other sources of organic gases as demonstrated by an air sample taken at the site.	___	___
(4) GC/MS system is in air conditioned room.	___	___
(5) Data system is in air conditioned room.	___	___
(6) Instruments, including GC/MS pumps, are vented into hoods or control devices.	___	___
(7) Laboratory has clean, neat appearance; movement and work are not impeded by clutter.	___	___
(8) All apparatus, instrumentation, bench tops, hoods, etc., are free of loose corrosion products and dust.	___	___
(9) All glassware is stored so as to be protected from airborne dusts.	___	___

Sample Check-In and Handling	YES	NO
(1) Each sample (Tenax GC® sampling tube) is checked for an Identification Number upon receipt	___	___
(2) The Identification Number of each sample is recorded in a sample logbook.	___	___
(3) Analysts have a list of the deadlines for analysis of samples received.	___	___
(4) Sample tubes are stored in a freezer reserved solely for Tenax GC® samples.	___	___

(5) What is the temperature of the freezer used for storage of Tenax sample tubes?

_____

(6) What is the maximum time allowed between preparation of a Tenax sampling tube and its use for sample collection?

_____

(7) What is the maximum time allowed between sample collection with a Tenax sampling tube and analysis of the contents of that tube? _____

(8) Samples are kept in a secure (locked) area.	___	___
(9) Samples are stored separate from standards.	___	___
(10) Sample collection date and sample volume are recorded in sample logbook.	___	___
(11) Separate sample logbooks are maintained for each sample site.	___	___

Sample Custody	YES	NO
(1) Sample Custodian has list of his (her) responsibilities in writing.	___	___
(2) Chain-of-custody forms are available for evaluation.	___	___
(3) The chain-of-custody forms accurately indicate the location of samples.	___	___

Equipment Testing and Maintenance	YES	NO
(1) Instrument inspection and maintenance records are available for review by evaluation personnel.	___	___
(2) Instrument-use logbook(s) maintained for the following:	___	___
GC/MS system	___	___
data system	___	___
(3) Laboratory utilizes instrument maintenance schedules.	___	___

Tenax GC®

Cleaning

(1) What procedure is used for washing the glassware used for Tenax GC® extraction, drying and storage? _____

_____

_____

_____

(2) To what temperature and for how long is the glassware heated?

_____

(3) What extraction procedure and solvents are used to clean the Tenax GC®?

_____

_____

_____

(4) What procedure is used to dry the extracted Tenax GC®?

_____

_____

_____

(5) What procedure is used to clean the glass wool used to hold Tenax GC® in place?

_____

_____

_____

(6) Describe the secondary container in which a packed Tenax sample tube is stored.

_____

_____

(7) How and when are the individual Tenax sample tubes labelled?

_____

(8) What information is placed on a Tenax sample tube label?

_____

(9) What procedure is used to check for Tenax sample tube contamination? _____

_____

_____

(10) What procedures are used for handling cleaned glassware and Tenax sampling tubes? _____

_____

Fortification (Spiking) by Gas Flowthrough

(1) Describe the nature of the connection between the standard gas source and the Tenax sampling tubes._____

_____

(2) At what rate is the standard gas passed through the Tenax sampling tubes? _____

_____

Fortification (Spiking) by Injection

(1) What procedures are used to minimize sample loss from the syringe after it is loaded with standard gas? _____

_____

_____

_____

(2) Describe the procedure used to fortify the Tenax GC® with the standard gas. _____

_____

_____

_____

(3) What procedures are used to clean the syringe after each injection? _____

_____

(4) What procedures are used to check syringes for cleanliness?

_____

_____

(5) What procedures are used to check the syringes for leaks?

_____

_____

_____

Storage

(1) Describe the environment (location) used for storage of Tenax sampling tubes.

_____

_____

(2) At what temperature are the Tenax sampling tubes stored? _____

_____

Calibration Gases

Preparation of Standard Organic Gas Mixtures
Static Dilution Bottle Method

(1) What procedure is used to determine the volume of the dilution bottle? _____

_____

(2) Describe the procedures used to clean the dilution bottle.

_____

_____

_____

(3) Describe the septum device (system) fitted to the dilution bottle.

_____

_____

(4) What is the minimum volume of liquid injected into the dilution bottle? _____

_____

(5) What procedures are used to clean the syringes used to withdraw sample from the dilution bottle? _____

_____

(6) At what temperature is the dilution bottle maintained? _____

_____

(7) What procedures are used to clean the syringes used to withdraw sample from the dilution bottle? _____

_____

Preparation of Standard Organic Gas Mixtures
Permeation Tube Method

(1) How often are the rates of the permeation tubes determined?

_____

(2) What level of repeatibility must a permeation tube show before it is used as a standard gas source? _____

_____

_____

(3) Describe the conditions used for storage of permeation tubes.

_____

_____

(4) What is the precision of the temperature of the permeation chamber? _____

(5) What is the rate of flow of dilution air passed through the permeation chamber? _____

_____

(6) Describe the construction of the permeation/dilution system.

_____

_____

_____

_____

(7) What procedure is used to check gas flows into and out of the permeation/dilution system? _____

_____

_____

(8) How often are gas flows into and out of the permeation/dilution system checked? _____

_____

(9) What is the precision of the gas flows into and out of the permeation/dilution system? _____

_____

(10) At what temperature is the dilution system maintained?

_____

_____

_____

(11) How are the Tenax sampling tubes attached to the dilution system? _____

_____

_____

(12) What is the rate of flow of the standard gas through the Tenax sampling tubes?

_____

(13) Describe the conditions used to store the fortified Tenax sampling tubes. _____

_____

_____

GC/MS Analysis

(1) Describe the column used in the GC/MS system. _____

_____

(2) At what temperature is the heating block of the thermal desorption unit maintained? _____

(3) What is the rate of flow of helium through the thermal desorption unit? _____

(4) What is the heating rate of the cryogenic trap for vaporization? _____

(5) At what temperatures are the GC injector and detector maintained? _____

(6) Describe the temperature program used for the GC.

_____

_____

(7) At what temperature is the MS source maintained?

_____

(8) What is the MS scan time? _____

(9) What is the MS scan range? _____

(10) Describe the data system used. _____

_____

_____

(11) Describe the procedure used for calibration. _____

_____

_____

(12) How many points are included in the calibration curves for each compound when using external standards for quantification? _____

(13) How often are calibration curves checked and/or new calibration curves acquired?

_____

(14) What is the mass range usually covered by the calibration curves? _____

(15) What are the precision control limits for slopes and intercepts of replicate calibration curves? _____

_____

(16) What are the precision control limits for relative retention times measured with PFT and/or PFB? _____

_____

(17) Describe the procedure used to determine detection limits.

_____

_____

_____

(18) What compounds are used to test the performance of the GC/MS system?

_____

_____

(19) Describe the procedure used to check column resolution.

_____

_____

_____

(20) Describe the procedure used to check the percent peak asymmetry factor. _____

_____

_____

(21) Typical analysis report includes the following:

	YES	NO
contract number and title	___	___
type of report	___	___
sequence number of report	___	___
period of performance being reported	___	___
contractor's name and address	___	___
report author's name(s)	___	___
report publication date	___	___
description of samples	___	___
data in tabular format	___	___
substances grouped by chemical class or group	___	___

Data Reduction and Validation	YES	NO
(1) Field data sheets are examined and corrected if obvious errors are noted.	___	___
(2) Values below quantification limits are stored in computer memory as calculated values.	___	___
(3) The data clerk submits quality control data sheet information and analytical data to the laboratory manager.	___	___

(4) What percent of the data entered into the computer is checked for reasonableness by the data clerk? _____

(5) What percent of all values in the data base are manually checked for calculation accuracy? _____

(6) What percent of sample results with extremely high concentrations are checked for calculation errors? _____

(7) How long are raw data, QC data, and reports stored beyond the termination of a typical analysis contract?

_____

Quality Control	YES	NO
(1) Calibration curve slope and intercept values are regularly reviewed by the Quality Assurance Officer as evidence for instrument control.	—	—
(2) QC charts are maintained for the following:		
resolution	—	—
percent peak asymmetry factor	—	—
peak areas of selected ions of performance evaluation compounds	—	—
PFT and/or PFB retention times	—	—
detection limits of system performance evaluation compounds	—	—
calibration curve coefficients	—	—

Corrective Action	YES	NO
(1) Contingency plans are available for corrective action resulting from:		
intramural or extramural performance audits	___	___
systems audits	___	___
interlaboratory performance audits	___	___
internal QA/QC checks	___	___
(2) Copies of corrective action procedures are available.	___	___
(3) The Quality Assurance Officer (QAO) is notified in writing of the need for and results of corrective action.	___	___

Cite examples: _____

_____

_____

(4) Corrective Action Request Forms are available to evaluation personnel. ___ ___

(5) Who in the organization besides the QAO is notified of the need for or the taking of corrective action?

_____

_____

(6) Describe criteria used to evaluate the efficiency of the corrective action. _____

_____

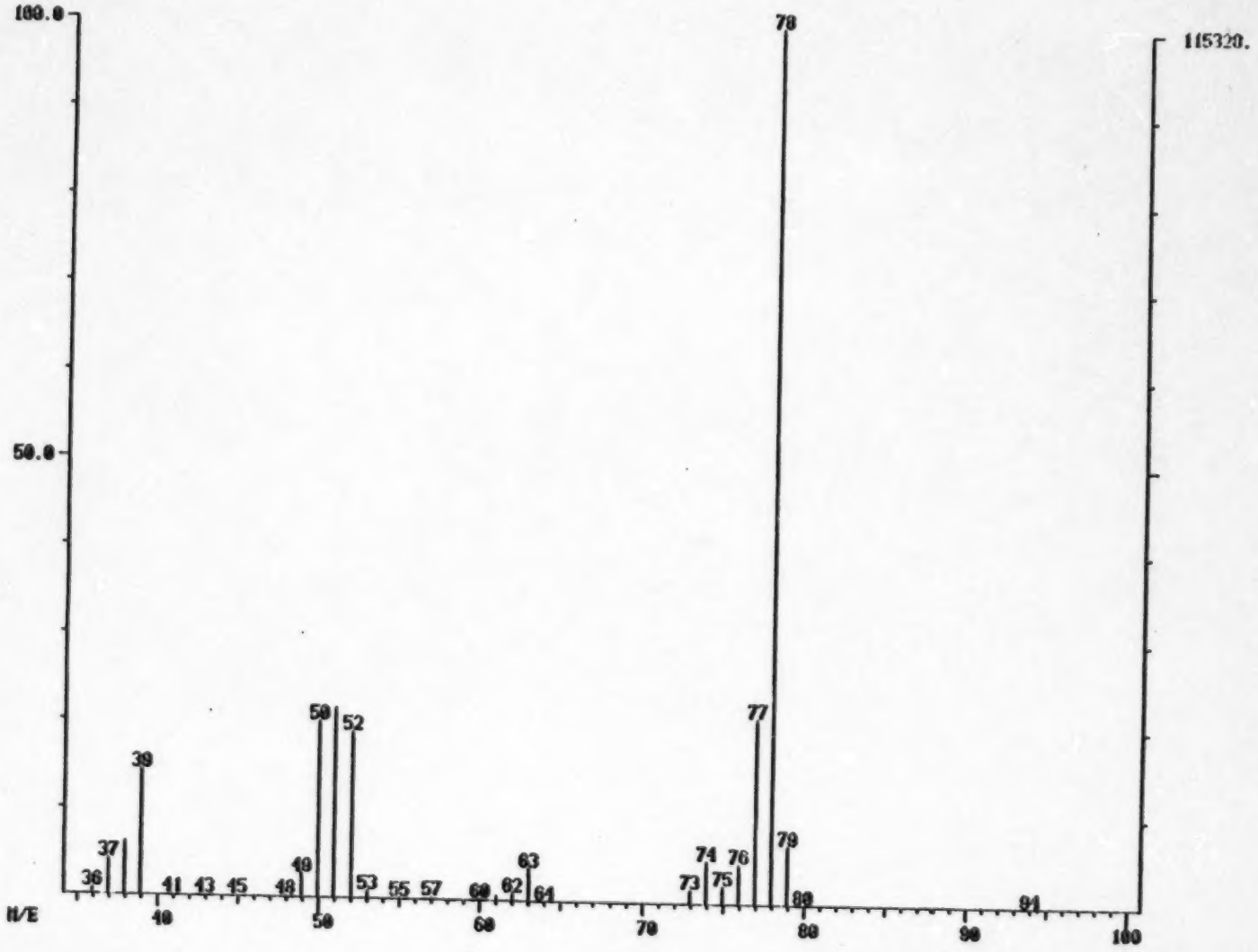
_____

_____

_____

APPENDIX B

Example Data



Mass Spectrum of Benzene

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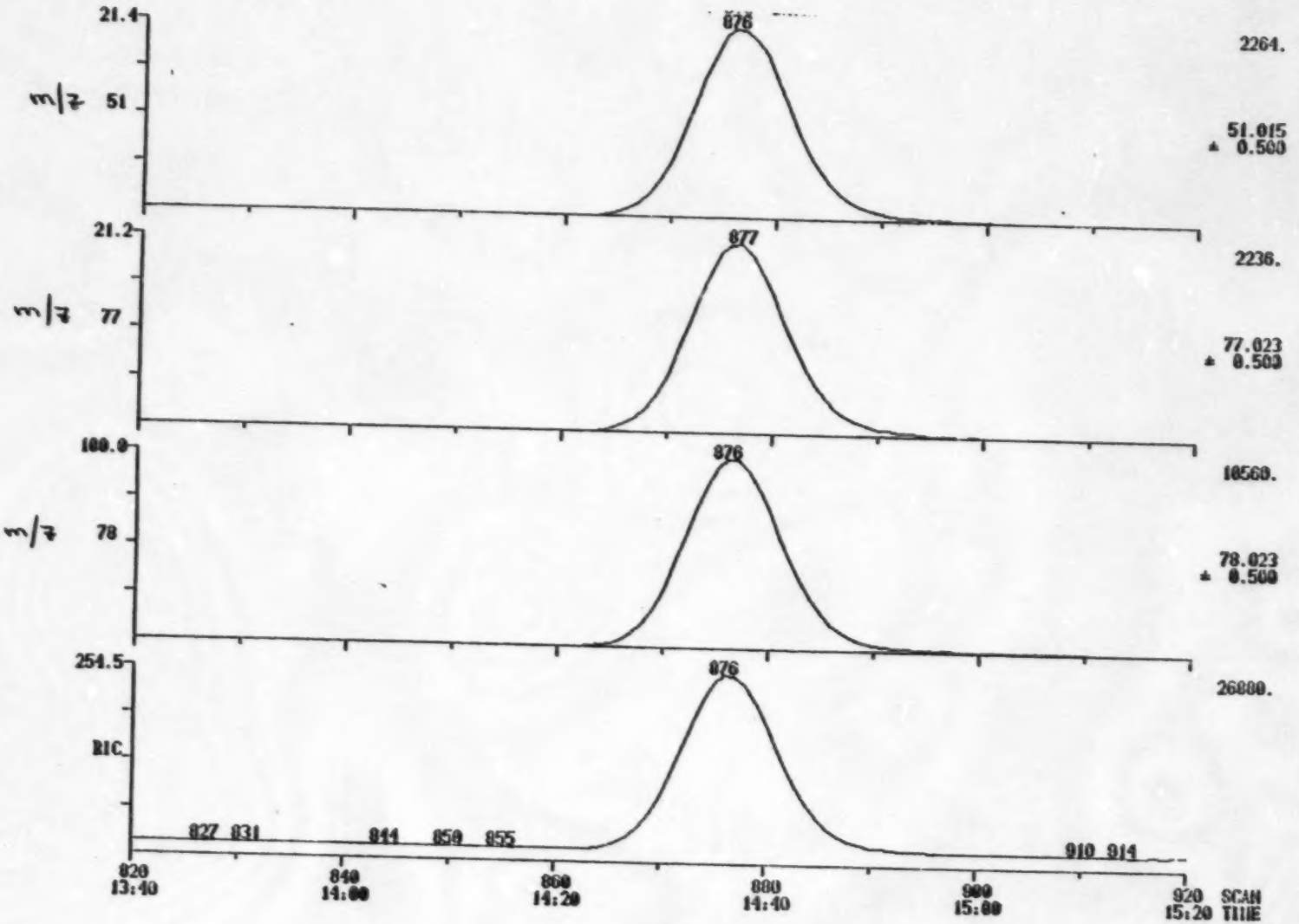
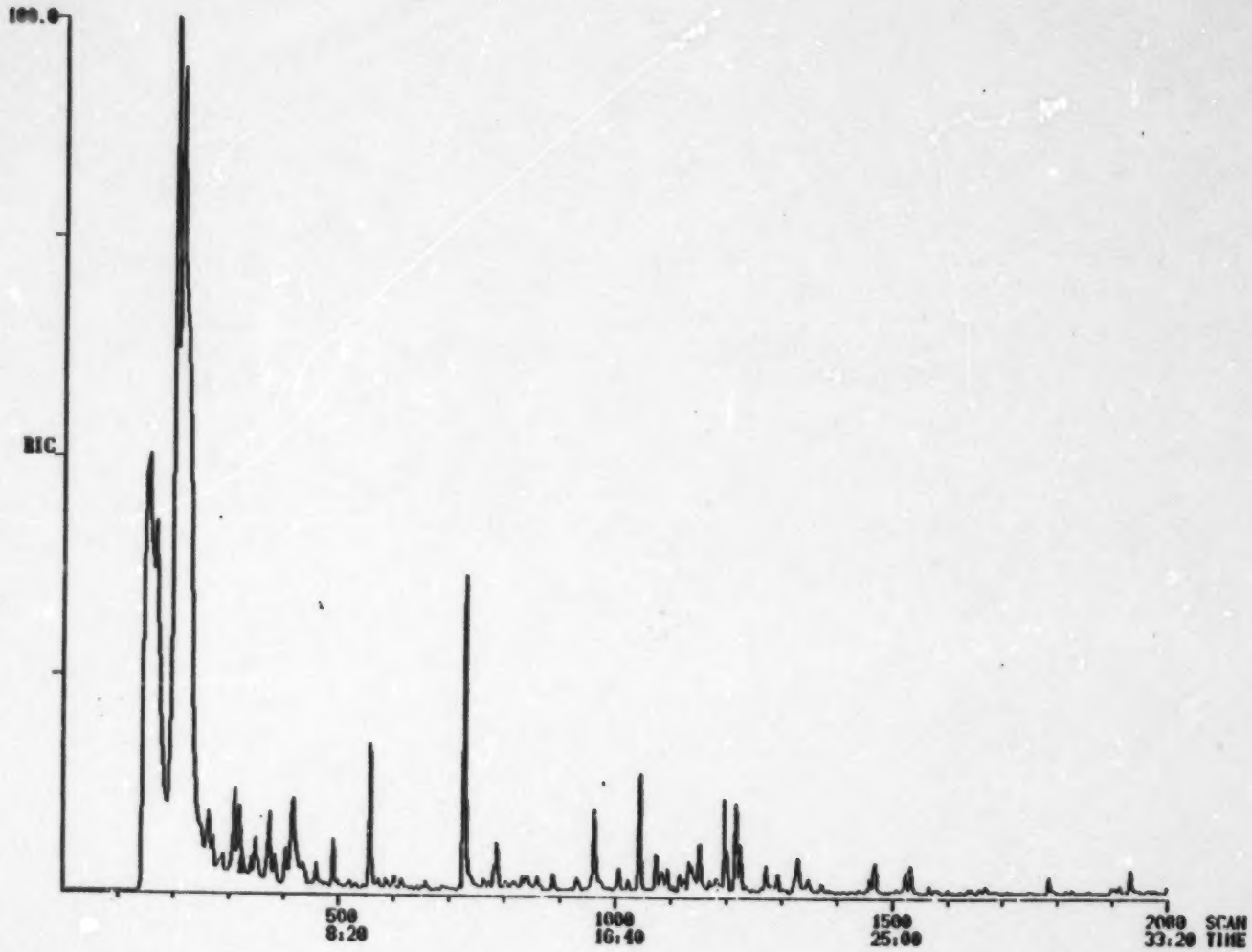
```
MASS LIST                          DATA: 4ZZZ3317 ● 877      BASE M/E:   78
08/11/82 19:25:00 + 14:37          CALI: FC431 ●   7         RIC:    272896.
SAMPLE: SAMPLE A●1
 ●867 TO ●888 SUMMED - ●848 TO ●856 - ●903 TO ●914

    36        0.00    0.00        0. MINIMA     MIN INTEN:      0.
    94                          ●   0 MAXIMA
  MASS        x RA    x RIC    INTEN.

 36.007  S    0.69    0.29      795.
 37.007       4.16    1.76     4792.
 38.007       6.08    2.57     7016.
 39.007  S   14.32    6.05    16512.
 41.00   S    0.17    0.07      193.
 42.00   S    0.03    0.01       39.
 43.00   S    0.14    0.06      157.
 45.00   S    0.09    0.04      104.
 49.00        0.12    0.05      144.
 49.00        2.73    1.16     3152.
 50.00       20.12    8.50    23200.
 51.00       21.67    9.16    24992.
 52.00       18.90    8.02    21800.
 53.00        0.85    0.36      984.
 55.00   S    0.09    0.04      104.
 56.00   S    0.02    0.01       26.
 57.00   S    0.25    0.10      284.
 60.00        0.09    0.04      108.
 61.00        0.54    0.23      620.
 62.00        0.79    0.34      915.
 63.00        3.71    1.57     4280.
 64.00        0.07    0.03       76.
 73.00        1.50    0.63     1720.
 74.00        4.90    2.07     5640.
 75.00        1.90    0.84     2200.
 76.00        4.61    1.95     5320.
 77.00       21.20    8.96    24440.
 78.00   S 100.00   42.26   115320.
 79.00        6.71    2.84     7744.
 80.20        0.03    0.01       39.
 94.00        0.03    0.01       40.
```

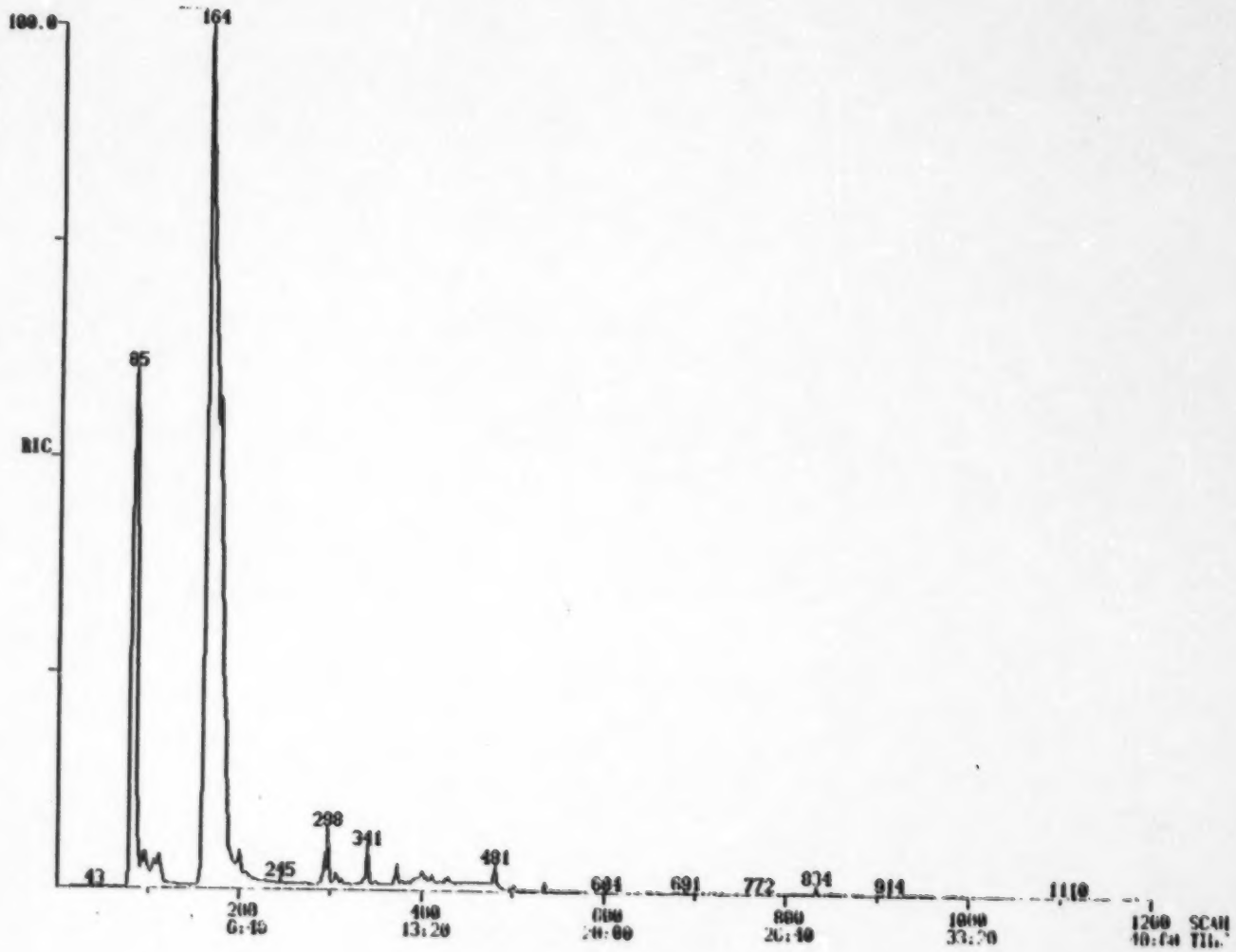
Typical Mass List - Benzene



Selected Ion Plots - Benzene



TIC Chromatogram of Tenax GC Field Blank



TIC Chromatogram of Tenax GC Laboratory Blank

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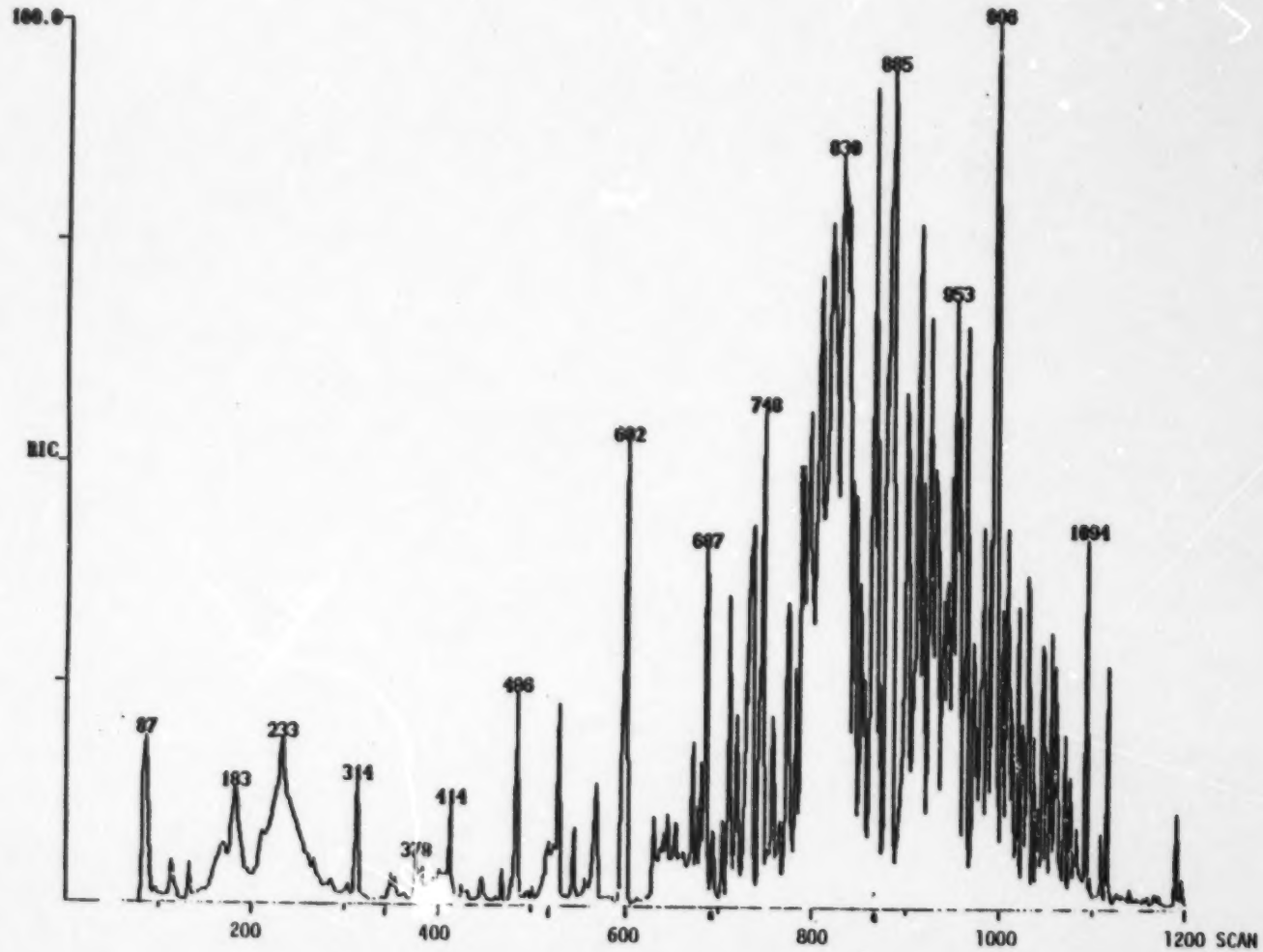

TIC Chromatogram of Tenax GC Field Sample

Tenax Batch _____
GC/MS Model No. FINN 3300

PF3 (ng) _____ Sampling Temp. (°F) _____ Date Collected _____
PFT (ng) _____ Sampling Volume _____ Date Analyzed _____
Collection Times: Start _____ Finish _____ Analyst ID _____

EP Code No.	TSO Code No.	Compound	M.W.	Scan No.	Ions	Areas	Ratios (2°/1°; 3°/1°) Th.	Obs.	Clean	ng	µg/m³
	18	Perfluorobenzene	186		186 117						
		Perfluorotoluene	236		69 79 93 117 148 167 186 217 236						
1	117	Vinylidene chloride	96		*61 96 98		.62 .38				
2	125	Chloroform	118		*83 85		.62				
3	133	1,2-Dichloroethane	98		*62 64		.32				
4	141	1,1,1-Trichloroethane	132		61 *97 99		.58 .62				
5	158	Benzene	78								
6	166	Carbon tetrachloride	152		*117 119		.95				
7	174	Trichloroethylene	130		*95 130 132		1.00 .95				
8	182	Bromodichloromethane	162		*83 129		.18				
9	190	Dibromochloromethane	206		127 *129		.78				
10	208	Toluene	92		91						
11	216	Tetrachloroethylene	164		164 *166		.78				
12	224	Chlorobenzene	112		*112 114		.32				
13	232	Bromoform	250		173						
14	240	Dibromochloropropane	234		155 *157		.78				
15	257	Styrene	104		104						
17	273	o & p-Dichlorobenzene	146		*146 148		.65				
18	281	p-Dichlorobenzene	146		*146 148		.65				
19	299	Ethylbenzene	106		*91 106		.32				
20	307	p-Xylene	106		*91 106		.58				
22	323	m & p-Xylene	106		*91 106		.66				
		d_6-Benzene	84		84						
		d_3-Bromoethane	113		113 115						

Example Data Reporting Form